

sent in urine is, however, so small that the precise nature of this substance has not as yet been determined.

Finally, the author points out an apparent connexion between this substance and alcohol. It was found that, after the elimination due to the ingestion of alcohol had ceased, the amount of this substance eliminated in a given time at first remained below the quantity normally excreted, and only gradually rose again to the normal standard. A careful study of this connexion may perhaps serve to throw some light upon the physiological action of alcohol.

III. "On the Action of Low Temperatures on Supersaturated Solutions of Glauber's Salt." By CHARLES TOMLINSON, F.R.S.  
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When a solution of the ordinary ten-atom hydrate of sodic sulphate, saturated at about 93° F., its maximum point of solubility, is boiled and filtered into a clean flask, which, being closed, is left to cool to 40° and under, a modified or seven-atom hydrate is formed at the bottom of the solution; this increases in quantity as the temperature falls, and passes into solution as the temperature rises; and, so far, the observation is supposed to be complete.

But if a supersaturated solution of Glauber's salt be reduced from ordinary atmospheric temperatures to low ones by means of a freezing-mixture of snow and salt, the results obtained are so remarkable that I venture to think a short statement of them may be worthy of a place in the 'Proceedings,' by way of addenda to Section II. of my second paper "On Supersaturated Saline Solutions," contained in the *Philosophical Transactions* for 1871, page 59.

A solution of one part Glauber's salt in one of water was boiled and filtered into a two-ounce flask that had been previously filled with strong nitric acid and well rinsed with clean water. The solution was again boiled in this flask, into which a thermometer was passed, the stem being surrounded by several turns of lamp-cotton, which served to close the flask as soon as it was removed from the source of heat.

Next day the flask was put into a freezing-mixture at about 15° F. The solution slowly sank to 19°, when there was an abundant deposit of crystals of a peculiar opaque white, not like the transparent octahedra that are thrown down when these solutions cool to 40° and under, but very much like the octahedral crystals formed during the cooling of a strong solution of sal-ammoniac. There were tufts of regular octahedra and fern-like crystalline forms. During their formation the thermometer rose to 26°. The flask was now transferred to water at 48°, when the opaque-white crystals broke up into an amorphous woolly mass. As the temperature of the solution rose to 40°, then for the first time the usual transparent octahedra of the anhydrous salt fell down. Next day the

flask was opened; crystallization of the ordinary salt set in from the surface, and the temperature rose from  $44^{\circ}$  to  $65^{\circ}$ .

Thus one more hydrate is added to those already known as belonging to this remarkable salt. It doubtless contains less water than the seven-atom hydrate; but I know of no method of testing its hydration, since its existence depends upon the low temperature, and shelter from the action of nuclei. In this way it resembles the various hydrates described in my paper in the 'Transactions.'

The solution was next made twice as strong as before, that is, two parts of Glauber's salt were dissolved in one part of water, and after boiling and filtering and reboiling as before, the flask was set aside to cool. When the thermometer marked  $42^{\circ}$ , the flask was put into the freezing-mixture. At  $38^{\circ}$  a few transparent octahedra were thrown down, and the heat-currents thereby liberated delayed the cooling. In fourteen minutes it reached  $26^{\circ}$ , and the transparent crystals at the bottom became opaque white. The thermometer was stationary during some minutes at  $26^{\circ}$ , when it began again to descend; but on agitating the flask in the freezing-mixture, crystals of the opaque-white salt were formed, and the temperature regained  $26^{\circ}$ , the solution above being bright and clear, and still supersaturated. In a few minutes crystallization set in from the surface, and the thermometer rose from  $26^{\circ}$  to  $53^{\circ}$ , the whole being now solid.

These opaque crystals resemble in texture newly formed white lead; and at whatever temperature they may be formed below  $26^{\circ}$ , their formation causes the thermometer to rise to  $26^{\circ}$ , and that, too, in solutions of 1 part, 2 parts, or 3 parts salt to one of water. This opaque salt is sometimes amorphous, and then it covers the surface of the flask like thick whitewash. This effect occurs when the flask is much agitated in the freezing-mixture.

The same flask (2 salt to 1 water) was reboiled without any addition of water, so that the solution was really stronger than that indicated. At  $40^{\circ}$  there was a fall of transparent anhydrous crystals. The solution was now purposely cooled very slowly, so that in half an hour it descended only  $3^{\circ}$ , namely, to  $37^{\circ}$ . There was now a considerable increase of the anhydrous salt so as to cover the bottom of the flask, and to rise a little way up the sides. The flask was transferred to a freezing-mixture at  $10^{\circ}$ ; when at  $33^{\circ}$  the anhydrous salt became opaque, doubtless from the fixation of a portion of water less than that required for the formation of the seven-atom salt. At  $24^{\circ}$  opaque tufts and fern-like crystals were formed. At  $22^{\circ}$  there was a sudden and copious deposit of this opaque-white hydrate; the thermometer rose to  $26^{\circ}$ , and then suddenly to  $52^{\circ}$ , when the whole mass was solid.

It is commonly supposed that the rise in temperature consequent on the solidification of a supersaturated solution is dependent on its mass; that when this is considerable, the rise in temperature is so too, but that when the mass is small there is but little heating. This does not accord

with my experience. Not much more than half an ounce of a comparatively weak solution of Glauber's salt, such as 1 salt to 1 water, may rise from  $20^{\circ}$  to  $56^{\circ}$  on suddenly becoming solid; and with 2 or 3 salt to 1 of water the rise may not be greater, especially if a considerable mass of the two abnormal hydrates be already formed, and only a small portion of the solution remain to become solid.

In another experiment, 3 parts salt to 1 of water were boiled and filtered into two test-tubes and one 2-ounce flask. One tube, on being put into the freezing-mixture, sank to  $35^{\circ}$ , when the solution suddenly became solid, and the thermometer rose to  $78^{\circ}$ . The other tube-solution threw down so large a quantity of anhydrous crystals as to prevent the reading of the thermometer. The solution in the flask threw down anhydrous crystals at  $44^{\circ}$ , and then sank very slowly to  $40^{\circ}$ , where it remained stationary upwards of ten minutes, in consequence of the liberation of heat-currents, occasionally rising to  $41^{\circ}$ . A large quantity of transparent crystals was now heaped up on the bulb of the thermometer; the temperature descended to  $38^{\circ}$ , with slight starts upwards; and in slowly descending to  $33^{\circ}$ , there was a large increase of the transparent crystals. At  $32^{\circ}$  the flask was transferred to a fresh freezing-mixture at  $10^{\circ}$ , and the solution slowly descended to  $22^{\circ}$ , when it was again removed to a fresh freezing-mixture, also at  $10^{\circ}$ . Soon a number of large fern-like crystals covered the side of the flask, starting, apparently, from the top of the copious deposit first produced, and rendering the upper part opaque in a well-defined line. The temperature rose to  $26^{\circ}$ , and continued there some minutes, when the solution suddenly crystallized, and the thermometer rose to  $48^{\circ}$ .

Supersaturated solutions of potash alum, exposed to low temperatures, behave much in the same way as the solutions of double salts described in my former paper. A solution of 300 grains of the salt in  $1\frac{1}{2}$  oz. of water, boiled and filtered into clean test-tubes, and, when cold, put into a freezing-mixture at about  $0^{\circ}$  F., displays the beautiful ivy-leaf kind of foliage, of a brilliant white colour, already referred to. The growth starts from the bottom or from the surface of the solution, or from both, and soon the whole solution becomes solid. If the tube be put into water at  $32^{\circ}$ , the solid rapidly melts, and the liquid is a clear bright supersaturated solution as before.

Löwel, in his first memoir (*An. de Ch. et de Ph.* 3 série, tome xxix.), found that when supersaturated solutions of Glauber's salt, in sealed tubes, were subjected to temperatures varying from  $-8^{\circ}$  to  $-10^{\circ}$  C., they often froze and burst the tubes. In one case, where the tube did not burst, the solution, in thawing, caused the state of supersaturation to cease. In another case the frozen solution thawed, and the liquor became supersaturated as before. Löwel could not reproduce this last effect, nor explain why the thawing should lead to the formation of the ten-atom salt. But as he did not know the conditions of clean and unclean, he was constantly looking out for some catalytic action in the sides of his vessels to explain the many

anomalous cases that occurred to him consequent on the use of vessels not chemically clean.

Among the numerous writers on the subject of supersaturation, I know of none that has noticed the formation of the second modified hydrate of sodic sulphate except M. Viollette, who, in a "Mémoire sur la Sursaturation" contained in the 'Annales Scientifiques de l'École Normale Supérieure' (tome troisième année, 1866), refers in about a dozen words, p. 223, to the formation of another hydrate, "qui cristallise difficilement en forme de choux-fleurs,"

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